1.1 g. (44%) of a liquid which consisted of equal amounts of benzaldehyde oxime and benzylamine as determined by v.p.c.

Treatment of N-Benzylhydroxylamine with Base.—To 0.5 g. (4.1 mmoles) of N-benzylhydroxylamine was added 10 ml. of 10% potassium hydroxide. The reaction mixture was refluxed for 1 hr. and then extracted continuously with pentane for 48 hr. Evaporation of pentane in a nitrogen stream gave 0.42 g. (84% of a liquid which consisted of equal amounts of benzaldehyde oxime and benzylamine as determined by v.p.c.

Preparation of Heptanal Oxime–Diborane Adduct (Isolation of Intermediate).—To a mixture consisting of 2.70 g. (21 mmoles) of analytically pure heptanal oxime and 30 ml. of Phillips pure grade pentane (99 mole % minimum) at 0° was introduced approximately 61 mmoles of gaseous diborane (366 mequiv. of hydride ion) over a 2-hr. period. During the first 0.5 hr. of addition, hydrogen (identified by mass spectrography) was evolved. The mixture was held at room temperature for 7 hr. following diborane addition. Removing pentane and excess diborane *in vacuo* and heating the residue at 80° (0.05 mm.) for 3 hr. afforded 3.0 g. of a viscous, translucent liquid: $\lambda_{\max}^{\text{neat}}$ 4.15 (BH), 5.95 (BH), and 6.2 μ (BN); n.m.r. 0.9 (CH_3, triplet) and 1.3 p.p.m. (CH_2, singlet).

Anal. Calcd. for $C_{28}H_{70}B_6N_4O_4$; C, 56.80; H, 11.80; B, 11.13; N, 9.47; mol. wt., 594. Found: C, 56.89; H, 11.64; B, 10.98; N, 9.28; mol. wt., 638 (in benzene).

Work-up of an aliquot of the heptanal oxime–diborane adduct by the usual procedure gave a 63.2% yield of **N-heptylhydroxylamine**.

O-Methyl 1,3-Diphenyl-2-propanone Oxime.—To a 500-ml. flask, equipped with a magnetic stirrer, were added 150 ml. of absolute ethanol, 10.2 g. (45.3 mmoles) of 1,3 diphenyl-2-propanone oxime, and 1.13 g. (45.3 mg.-atoms) of metallic sodium, the latter in small pieces. After all of the sodium had dissolved, 6.4 g. (45 mmoles) of methyl iodide dissolved in 25 ml. of absolute ethanol was added dropwise, and the reaction mixture was stirred for 18 hr. at room temperature and then refluxed for 2 hr. The ethanol was stripped off *in vacuo* and the remaining material was extracted with anhydrous ether. Evaporating the ether extract in a nitrogen stream and distilling gave 1.50 g. (14%) of **O-methyl 1,3-diphenyl-2-propanone oxime**: b.p. 100–110° (0.3 mm.); $n^{20}D$ 1.5596; $\lambda_{\max}^{\text{neat}}$ 3.3 and 3.4 (CH), 6.2 (C═N and phenyl), and 9.55 μ (unassigned); n.m.r. 3.4 and 3.6 [$CH_2C(N)CH_2$, two singlets], 3.95 (OCH_3, singlet), and 7.3 p.p.m. (aromatic H, singlet).

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.85. Found: C, 79.94; H, 7.19; N, 6.08.

Reaction of Diborane with O-Methyl 1,3-Diphenyl-2-propanone Oxime.—To 2.88 g. (12 mmoles) of O-methyl 1,3-diphenyl-2-propanone oxime at 0° was introduced by means of a hypodermic syringe 9.0 ml. of a 2.13 *M* solution of borane in THF at such a rate that the temperature did not exceed 10°. Continuing the reaction for 12 hr. at ambient temperature, removing the solvent *in vacuo*, and lowering the temperature to 0° was followed by the addition of 10 ml. of 10% potassium hydroxide by means of a syringe, at such a rate that the temperature did not exceed 5°. Then refluxing the reaction mixture 1 hr., extracting with pentane for 48 hr., and removing the solvent in a nitrogen stream gave 2.09 g. (82.6% crude yield) of 1,3-diphenyl-2-propylamine. Addition of an aliquot of the crude amine to a saturated ethanolic picric acid solution afforded, after two recrystallizations from absolute ethanol, **1,3-diphenyl-2-propylamine picrate**, m.p. 193° dec. (lit.[30] m.p. 193°).

Anal. Calcd. for $C_{21}H_{20}N_4O_7$: C, 57.37; H, 4.58; N, 12.72. Found: C, 57.73; H, 4.85; N, 12.42.

Bubbling anhydrous hydrogen chloride through an ether solution of the crude amine gave **1,3-diphenyl-2-propylamine hydrochloride**, m.p. 200–202° dec. (lit.[30] m.p. 202°).

Acknowledgment.—We wish to thank the Office of Naval Research for financial support of this work.

[30] B. B. Dev and V. S. Ramanathan, *Proc. Natl. Inst. Sci. Ind.*, **9**, 193 (1943); *Chem. Abstr.*, **43**, 5027*b* (1946).

Diborane Reduction of Nitro Salts. A New Synthesis of N-Monosubstituted Hydroxylamines

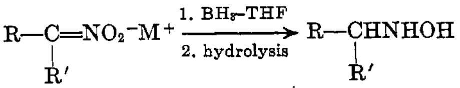
H. Feuer, R. S. Bartlett, B. F. Vincent, Jr., and R. S. Anderson

Department of Chemistry, Purdue University, Lafayette, Indiana

Received May 10, 1965

Nitro compounds which are unaffected by diborane interact readily in the form of their salts with this reagent. The reaction leads to intermediates which on basic or acid hydrolysis afford N-monosubstituted hydroxylamines in yields of 30–60%.

A new synthesis of N-monosubstituted hydroxylamines by reduction of the corresponding aldoximes and ketoximes with diborane in tetrahydrofuran has recently been communicated.[1,2] This paper reports on another new and convenient route to hydroxylamines. It has been found that diborane, which does not affect nitro compounds,[3] reduces salts of primary and secondary nitro compounds[4] to the corresponding N-monosubstituted hydroxylamines.[5]



$$\underset{\displaystyle R'}{R\text{—}C}{=}NO_2^-M^+ \xrightarrow[\text{2. hydrolysis}]{\text{1. }BH_3\text{–THF}} \underset{\displaystyle R'}{R\text{—}CH}NHOH$$

R = H or alkyl; R′ = alkyl or aryl; M = Li, K, or NH_4

Results and Discussion

The procedure was similar to that utilized in the reduction of oximes.[2] As shown in Table I, the reduction of aliphatic and alicyclic nitronates gave intermediates which on basic or acidic hydrolysis afforded the corresponding N-monosubstituted hydroxylamines in 30–60% yield. Primary nitronates with the exception of potassium cyclohexylmethanenitronate gave somewhat lower yields than secondary nitronates. It was established that the yield of hydroxylamine was essentially independent of the nature of the cation, for lithium, potassium, and ammonium cyclohexanenitronate were converted to N-cyclohexylhydroxylamine in essentially the same yield.

The reduction of potassium phenylmethanenitronate with diborane gave N-benzylhydroxylamine (I) in 48% yield when the intermediate was hydrolyzed in acid medium. On basic hydrolysis, I underwent a disproportionation reaction to benzylamine and benzaldehyde oxime. This disproportionation was previously

---

[1] H. Feuer and B. F. Vincent, Jr., *J. Am. Chem. Soc.*, **84**, 3771 (1962).

[2] H. Feuer, B. F. Vincent, Jr., and R. S. Bartlett, *J. Org. Chem.*, **30**, 2877 (1965).

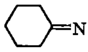
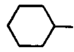
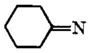
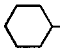
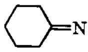
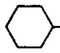
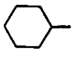
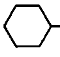
[3] H. C. Brown, "Hydroboration," W. A. Benjamin, Inc., New York, N. Y., 1962, p. 249.

[4] The term nitronate is used throughout to denote these compounds.

[5] Other reported methods of preparing hydroxylamines are presented in ref. 2.

TABLE I

DIBORANE REDUCTION OF ALKYLNITRONATES

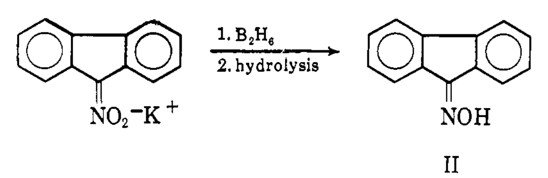
Nitro salt[a]	Hydroxylamine	M.p., °C.	Yield, %
$H_3CCH_2C(CH_3){=}NO_2^-Li^+$	$H_3CCH_2CH(CH_3)NHOH$[b]	67	49.4
$H_3C(CH_2)_2CH{=}NO_2^-K^+$	$H_2C(CH_2)_3NHOH$	54	32
 $=NO_2^-Li^+$	 $-NHOH$[c,d]	140	56
 $=NO_2^-K^+$	 $-NHOH$[e]	140	50.3
 $=NO_2^-NH_4^+$	 $-NHOH$	140	53
$H_3C(CH_2)_5CH{=}NO_2^-K^+$	$H_3C(CH_2)_6NHOH$	62	32
 $-CH{=}NO_2^-K^+$	 $-CH_2NHOH$[f]	62	62.4
$C_6H_5CH_2CH{=}NO_2^-K^+$	$C_6H_5CH_2CH_2NHOH$[g]	83	39

[a] 20 mmoles and an excess of diborane were employed. The reaction time was 20 hr. at 25°. [b] 74.0 mmoles of hydride ion was consumed. [c] G. Vavon and A. L. Berton [*Bull. soc. chim. France*, [4] **37**, 301 (1925)] reported m.p. 142°. [d] 64.0 mmoles of hydride ion was consumed. [e] 65.4 mmoles of hydride ion was consumed. [f] Calcd. for $C_7H_{15}NO$: C, 65.14; H, 11.64; N, 10.65. Found: C, 65.48; H, 11.40; N, 10.75. [g] Calcd. for $C_8H_{11}NO$: C, 70.07; H, 8.03; N, 10.21. Found: C, 69.74; H, 8.21; N, 10.70.

observed on basic hydrolysis of the reduction product from benzaldehyde oxime and diborane.[2,6]

In the reduction of nitronates with diborane, it was established that 3 equiv. of hydride ion per mole of nitronate were consumed and that essentially no evolution of hydrogen occurred prior to the hydrolysis of the intermediate. This is in contrast to the diborane reductions of oximes[2] where 1 mole of hydrogen per mole of oxime was evolved prior to hydrolysis and where a total of 1 equiv. of hydride ion was taken up in the reduction.

There is some evidence that the reduction of a nitronate with diborane to a hydroxylamine occurs stepwise *via* an oxime derivative. For the reduction of potassium 9-fluorenenitronate did not lead to N-9-fluorenehydroxylamine but gave instead 9-fluorenone oxime (II) in 39% yield. It was previously established that II was not affected by diborane.[2]



II

Another product of the reaction was 9,9′-dinitro-9,9′-bifluorene (III) which precipitated after acidification of the alkaline reaction mixture. Compound III was probably formed by oxidative dimerization of 9-acinitrofluorene[7] which derived from unreacted potassium salt on acidification.

As in the case of the oxime–diborane reduction, intermediates that remained after removal of excess diborane and THF contained active hydride in that hydrogen was evolved on addition of water. These intermediates were solids; in the case of the intermediate that was formed in the reaction of diborane with ammonium cyclohexanenitronate, it was established that the cation was still present, for only after treatment with base was ammonia liberated. In contrast, ammonium cyclohexanenitronate itself is rather unstable and evolves ammonia at ambient temperatures.

Experimental

Apparatus.—All reductions were carried out in a 3-necked, 50-ml. flask, equipped with a magnetic stirrer, thermometer, and a serum cap. A static pressure of high-purity nitrogen was maintained throughout the reaction by means of a Y-tube, connected from the top of the condenser, to a source of nitrogen and an acetone trap. All components of the system were dried at 150° for at least 4 hr. prior to use and flushed with nitrogen while cooling.

Hydrogen evolution was measured by attaching a gas buret through a Dry Ice trap to the outlet of the condenser.

Reagents.—Diborane was generated as described by Brown and solutions of diborane in tetrahydrofuran (THF) were prepared and standardized.[8] All nitro compounds were distilled *in vacuo* prior to use. THF was purified by the method of Feuer and Savides.[9]

Preparation of Alkylnitronates.—The following experiment is typical of the procedure employed. Into a 500-ml., 3-necked flask equipped with a stirrer, condenser, and addition funnel were placed 200 ml. of absolute ethanol and 7.8 g. (0.14 mole) of potassium hydroxide. After all of the potassium hydroxide had dissolved, 22 g. (0.17 mole) of nitrocyclohexane was added over a 1-hr. period and the mixture was stirred for 24 hr. at room temperature. Concentrating the reaction mixture to 20 ml. by removing ethanol on a Rinco evaporator gave a precipitate upon addition of 500 ml. of anhydrous ether. Filtration under nitrogen and drying *in vacuo* gave 15.3 g. (65.4%) of **potassium cyclohexanenitronate**, $\lambda_{\max}^{\text{neat}}$ 6.24 μ (C=N).

Anal. Calcd. for $C_6H_{10}NO_2K$: mol. wt.,[10] 161. Found: mol. wt., 168.

Lithium salts were prepared in the same manner except that lithium wire was employed.

Ammonium Cyclohexanenitronate.—Into an oven-dried, 100-ml., 3-necked flask, equipped with a Dry Ice condenser, thermometer, gas inlet tube, and magnetic stirrer were introduced 12.9 g. (0.1 mole) of nitrocyclohexane, 50 ml. of anhydrous ether, and approximately 25 ml. of liquid ammonia. The reaction mixture was stirred for 8 hr. at −33° and the excess ammonia allowed to evaporate at 0°. Filtering the mixture at 0° under nitrogen and drying in a nitrogen stream gave 13.8 g. (94.5%) of **ammonium cyclohexanenitronate**, $\lambda_{\max}^{\text{Nujol}}$ 6.25 μ (C=N).

When ammonium cyclohexanenitronate was allowed to stand in air at ambient temperature, ammonia was evolved.

Potassium 9-Fluorenenitronate.—Essentially the method of Feuer, *et al.*, was followed.[11] Into an oven-dried, 500-ml., 3-necked flask equipped with a thermometer, stirrer, and addition funnel were placed 180 ml. of dry THF and 48.0 g. (0.43 mole) of potassium *t*-butoxide. The solution was cooled to −40° and 33.2 g. (0.2 mole) of fluorene, dissolved in 150 ml. of THF, was added over a 0.5-hr. period followed by the addition of 23 g. (0.22 mole) of amyl nitrate. The reaction mixture was stirred at −40° for 1 hr., allowed to warm to 20°, and then filtered. Washing the filter cake with absolute ether, drying *in vacuo*, and recrystallizing from isopropyl alcohol afforded 18.5 g. (37.2%) of **potassium fluorenenitronate**.

Anal. Calcd. for $C_{13}H_8KNO_2$: C, 62.65; H, 3.21; K, 15.66; N, 5.62; mol. wt., 238. Found: C, 62.84; H, 3.65; K, 15.50; N, 5.53; mol. wt., 249.[10]

Reaction of Diborane with Alkylnitronates.—The following experiment is typical of the procedure employed. To 3.34 g. (20 mmoles) of potassium cyclohexanenitronate at 0° was introduced by means of a hypodermic syringe 23 ml. of a 2.18 *M* solution of borane in THF, at such a rate that the tempera-

---

[6] In contrast to N-benzylhydroxylamine, N-β-phenylethylhydroxylamine does not undergo disproportionation in alkaline medium.

[7] J. P. Freeman and K. S. McCallum, *J. Org. Chem.*, **21**, 472 (1956).

[8] H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **81**, 6428 (1959).

[9] H. Feuer and C. Savides, *ibid.*, **81**, 5826 (1959).

[10] H. Feuer and B. F. Vincent, Jr., *Anal. Chem.*, **35**, 598 (1963).

[11] H. Feuer, J. W. Shepherd, and C. Savides, *J. Am. Chem. Soc.*, **78**, 4364 (1956).

ture did not exceed 10°. Continuing the reaction for 20 hr. at ambient temperature, removing the solvent *in vacuo*, and lowering the temperature to 0° was followed by addition of 10 ml. of 10% potassium hydroxide, by means of a syringe, at such a rate that the temperature did not exceed 5°. (*Caution!* The first few drops of base should be added slowly because a considerable exotherm develops.) Then refluxing the reaction mixture for 1 hr., extracting with pentane for 90 hr., removing the solvent in a nitrogen stream, and subliming the residue at 60° (0.1 mm.) gave 1.16 g. (50.3%) of **N-cyclohexylhydroxylamine**, m.p. 140°.

Similarly, treating 3.34 g. (20 mmoles) of potassium cyclohexanenitronate with 28 ml. (130.2 mequiv. of hydride ion) of a borane–THF solution and keeping the reaction mixture for 20 hr. at ambient temperature resulted in the evolution of 1.8 mmoles of hydrogen.

Hydrolyzing the reaction mixture at 0° with 3 ml. of water, which was added slowly by means of a syringe, and then refluxing for 30 min. gave 63.0 mmoles of hydrogen. Removing THF *in vacuo*, adding 10 ml. of 10% potassium hydroxide at 0° to the residue, and refluxing for 1 hr. gave no more hydrogen. The total amount of hydrogen evolved was 64.8 mmoles, indicating that 3.2 equiv. of hydride was consumed in the reaction.

N-Benzylhydroxylamine.—To 3.50 g. (20 mmoles) of potassium phenylmethanenitronate at 0° was introduced by means of a hypodermic syringe 14 ml. of a 1.7 *M* solution of borane in THF at such a rate that the temperature did not exceed 10°. Continuing the reaction for 24 hr. at ambient temperature, removing the solvent *in vacuo*, and lowering the temperature to 0° was followed by the addition of 10 ml. of 20% hydrochloric acid by means of a syringe, at such a rate that the temperature did not exceed 5°. The reaction mixture was refluxed for 1 hr. while maintaining pH 1, made basic with 10% potassium hydroxide at 0°, and extracted with pentane for 72 hr. Removing the solvent in a nitrogen stream and subliming the residue at room temperature (0.2 mm.) gave 1.18 g. (48.1%) of **N-benzylhydroxylamine**, m.p. 57°.

Reduction of Potassium Fluorenitronate.—To 4.98 g. (20 mmoles) of potassium fluorenenitronate at 0° was introduced by means of a hypodermic syringe 27 ml. of a 1.86 *M* solution of borane in THF at such a rate that the temperature did not exceed 10°. Continuing the reaction for 12 hr. at ambient temperature, removing the solvent *in vacuo*, and lowering the temperature to 0° was followed by the addition of 10 ml. of 10% potassium hydroxide by means of a syringe, at such a rate that the temperature did not exceed 5°. Then refluxing the reaction mixture for 1 hr., extracting with pentane for 72 hr., removing the solvent in a nitrogen stream, and subliming the residue at 80° (0.2 mm.) gave 1.53 g. (39.2%) of **fluorenone oxime**, m.p. 195°. A mixture melting point determination with an authentic sample of fluorenone oxime showed no depression.

Acidification of the alkaline aqueous reaction mixture at 0° with 10% sulfuric acid and fitration of the precipitate gave 1.71 g. (40.6%) of **9,9′-dinitro-9,9′-bifluorene**: m.p. 163°; after recrystallization from absolute ethanol, m.p. 180° (lit.[12] m.p. 184°); $\lambda_{\max}^{\text{Nujol}}$ 6.4 μ (NO_2).

Acknowledgment.—We wish to thank the Office of Naval Research for financial support of this work.

---

[12] C. D. Nenitzescu, *Ber.*, **62**, 2669 (1929).

Solvolysis of *exo*-Norbornyl *p*-Trifluoromethylthionbenzoate

STANLEY G. SMITH[1] AND JOHN P. PETROVICH[2]

Noyes Chemical Laboratory, University of Illinois, Urbana, Illinois 61803

Received April 14, 1965

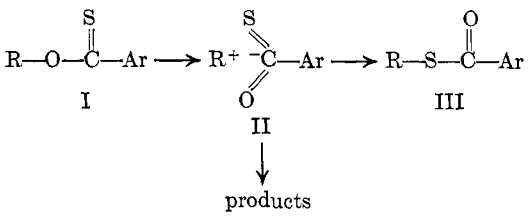
The rates of solvolysis of *exo*-norbornyl *p*-trifluoromethylthionbenzoate in acetic acid and aqueous ethanol were measured. It was found that in acetic acid at 140.0° the rate of loss of optical activity was the same as the rate of disappearance of the thion ester indicating that ion-pair return by oxygen to carbon 1 is not important with this system. The thiol ester produced in 16% yield was found to be at least 97% racemic indicating that the *exo*-norbornyl cation is symmetrical toward ion-pair return on sulfur.

Ionization rates often exceed the rate of formation of products in limiting solvolysis reactions because ion-pair return regenerates the starting material.[3] An understanding of structural effects on reactivity requires methods of measuring ionization rates in addition to total solvolysis rates.

Rate constants corresponding to ionization have been determined for systems in which heterolysis produces a carbonium ion in which two centers are made equivalent by participation[4,5] or where the first carbonium ion formed has rearranged[6] so that ion-pair return gives a new species of markedly different reactivity from the starting material.

With one-center carbonium ions in nonrearranging systems, scrambling of centers in the leaving group has recently been used as a measure of the lower limit to the ionization rate. For example, Goering,[7] Winstein,[8] and Swain[9] have used the scrambling of ^{18}O-labeled carbonyl and acyl oxygens in benzoate esters to estimate ionization rates. Darwish[10a] and co-workers have employed the reaction of sulfinate esters to give sulfones and solvolysis products, and Fava has studied the isomerization of thiocyanates to isothiocyanates.[10b]

We have used thion esters[11,12] I in studying solvolysis reactions since ionization would initially form an ion pair such as II in which it would be expected that ion-pair return would occur predominately on sulfur to produce the relatively stable thiol ester[11] III. With benz-



---

[1] Alfred P. Sloan Fellow.

[2] National Science Foundation Predoctoral Fellow.

[3] See, *e.g.*, A. Streitwieser, Jr. "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962.

[4] D. J. Cram, *J. Am. Chem. Soc.*, **86**, 3767 (1964).

[5] S. Winstein, E. Clippinger, R. Howe, and E. Vogelfanger, *ibid.*, **87**, 376 (1965).

[6] A. H. Fainberg and S. Winstein, *ibid.*, **79**, 1608 (1957).

[7] H. L. Goering and J. F. Levy, *ibid.*, **86**, 120 (1964).

[8] S. Winstein and B. R. Appel, *ibid.*, **86**, 2718 (1964).

[9] C. G. Swain and G. Tsuchihashi, *ibid.*, **84**, 2021 (1962).

[10] (a) D. Darwish and E. A. Preston, *Tetrahedron Letters*, **No. 2**, 113 (1964). (b) A. Fava, A. Iliceto, A. Ceccon, and P. Koch, *J. Am. Chem. Soc.*, **87**, 1045 (1965).

[11] S. G. Smith, *Tetrahedron Letters*, **No. 21**, 979 (1962).

[12] Part of this work has appeared in preliminary form: S. G. Smith and J. P. Petrovich, *ibid.*, **No. 45**, 3363 (1964).